

# PATENT SPECIFICATION

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## DRAWINGS ATTACHED

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## (54) PROCESS FOR THE PREPARATION OF CHROMIUM PENTOXIDE AND FERROMAGNETIC CHROMIUM DIOXIDE MADE THEREFROM

(71) We, RCA CORPORATION, a corporation organised under the laws of the State of Delaware, United States of America, of 30 Rockefeller Plaza, City and State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a novel process for the preparation of chromium pentoxide which chromium pentoxide is subsequently reduced to form ferromagnetic chromium dioxide which is useful in magnetic recording elements.

In recent years, processes have been described for the preparation of ferromagnetic chromium dioxide by thermal treatment of chromium trioxide in the presence of aqueous media. In addition, a process has been described for the preparation of ferromagnetic chromium dioxide by thermal treatment of chromium pentoxide in the presence of an aqueous medium. These processes provide ferromagnetic chromium dioxide in a variety of forms possessing a wide range of magnetic properties. However, such products have tended to be heterogeneous in particle size at least to an extent which has hindered realization of optimum properties in such application as magnetic recording members. In addition, the broad band bias noise of recording members such as recording tape, made from chromium dioxide prepared from these prior art methods has been relatively high and in some cases the coercive force and the saturation magnetization of the ferromagnetic chromium dioxide has been lower than desirable for use in recording elements.

The present invention provides a process for the preparation of chromium pentoxide. Improved chromium dioxide may be prepared from this pentoxide.

According to the invention we provide a process of preparing chromium pentoxide, comprising heating chromium trioxide at

atmospheric pressure in an atmosphere containing free oxygen with a temperature schedule controlled such that no part of the heated mass has a temperature of more than 15°C. above the control temperature, said control temperature not exceeding 350°C.

In the accompanying drawing:

Figures 1—3 are graphical representations of the particle size distribution of ferromagnetic chromium dioxide prepared by the novel process compared with chromium dioxide prepared outside the novel process.

One of the important recording characteristics of magnetic tape is broad band bias noise. It has surprisingly been found that the broad band bias noise of magnetic tape comprised of ferromagnetic chromium dioxide dispersed in a binder, is extremely sensitive to the temperature-time cycle used in the preparation of chromium pentoxide, which is a precursor for the preparation of ferromagnetic chromium dioxide. In fact, the procedure for the preparation of the chromium pentoxide has been found to have more of an effect on this property of magnetic tape than variations in the procedure for the synthesis of the magnetic chromium dioxide from the pentoxide.

It has also been found that this broad band noise and other magnetic characteristics, such as coercive force, are related to the particle size distribution and shape of the magnetic chromium dioxide particles. These parameters are related to the preparation of the chromium pentoxide starting material and often are related in a manner not detectable by chemical analysis of the pentoxide. However, in some cases, when proper temperature control is not maintained there may be Cr<sub>2</sub>O<sub>3</sub> formed during the reaction. The presence of this trioxide indicates an extremely poor temperature control, and the magnetic CrO<sub>2</sub> made from such a material will have poor particle size distribution and will be diluted by the nonmagnetic Cr<sub>2</sub>O<sub>3</sub>. Magnetic tape comprised of chromium dioxide prepared from chromium pentoxide as disclosed herein, has improved broad band

[Price 25p]

bias noise levels with no change in coercive force and a narrower range of particle size distribution, as compared to similar tapes comprised of chromium dioxide made by prior art techniques.

Typically, chromium pentoxide is prepared, according to the novel method, by heating  $\text{CrO}_3$  under flowing oxygen gas at atmospheric pressure to a final maximum temperature of about  $350^\circ\text{C}$ . It is critical that a careful and slow heating cycle be employed to prevent the exothermic decomposition of the  $\text{CrO}_3$  from causing a temperature deviation or spike of greater than  $15^\circ\text{C}$ . from the control temperature of the furnace. Temperature spikes in the chromium trioxide reactant and the chromium pentoxide product, hereinafter termed the reaction mixture, of greater than  $15^\circ\text{C}$ . can cause undesirable particle size distribution of the magnetic chromium dioxide prepared from the pentoxide. Where the temperature spikes cause localized heating of greater than  $360^\circ\text{C}$ ., non-magnetic  $\text{Cr}_2\text{O}_3$  will be produced which will remain throughout the synthesis of the ferromagnetic chromium dioxide, thereby contaminating and diluting that material.

One especially critical time during the heating cycle for the preparation of chromium pentoxide occurs around and above the melting point of the  $\text{CrO}_3$  starting material, that is, from about  $196^\circ\text{C}$ . to about  $250^\circ\text{C}$ . The temperature of the reactant should preferably be held within this range for several hours after all the  $\text{CrO}_3$  has completely melted. This is due to the fact that exothermic decomposition of the  $\text{CrO}_3$ , probably to  $\text{Cr}_2\text{O}_3$ , occurs within this temperature range. Typically, the heating cycle time may involve about 21 days for the preparation of a twenty-three pound batch of  $\text{Cr}_2\text{O}_3$  and five days for the preparation of a 3.5 pound batch.

#### (a) Preparation of Chromium Pentoxide

##### EXAMPLE I

675 grams of ACS reagent grade chromium trioxide is placed in a Pyrex (Registered Trade Mark) tube and heated in air in a vertical resistance-heated tube furnace. The following heating cycle is employed. The material is first gradually heated to  $200^\circ\text{C}$ . over a period of one hour. The temperature of the material is held at  $200^\circ\text{C}$ . for a period of 24 hours after which time the temperature is raised to  $250^\circ\text{C}$ . over a 30 minute period. The material is held at the  $250^\circ\text{C}$ . temperature for 24 hours, after which time the temperature is gradually raised to  $340^\circ\text{C}$ . over a period of one hour. Thereafter the temperature is held at  $340^\circ\text{C}$ . for a 12 hour period, after which time the material is allowed to cool to room temperature. By following this heating cycle, one can prevent the material from exceeding the control temperature by more than  $10^\circ\text{C}$ . for a batch of this particular size.

The product of this reaction is a hard black cake which is broken up and ground into a powder. The powder is then washed several times with distilled or deionized water and filtered between washings. It is preferable to wash the material either until the filtrate is clear or until the pH of the filtrate reaches about pH 4. The water washing is followed with an acetone wash after which the material is dried in air or vacuum at  $70^\circ\text{C}$ . The chromium pentoxide formed by this procedure is generally non-stoichiometric and is in the form of rectangular platelets which range up to about 0.5 microns by 0.5 microns by .05 microns in length, width and thickness, respectively.

##### EXAMPLE II

1590 grams of ACS reagent grade chromium trioxide is heated in a pyrex tube in a vertical resistance type tube furnace. An atmosphere of pure oxygen gas is maintained in the chamber by a continuous flow of about 0.5 cubic feet per minute through the chamber. In order to insure that the material does not exceed the controlled operating temperature by more than 15 degrees centigrade, the temperature of the material is monitored by thermocouples placed at the top, middle, and bottom of the material in the Pyrex tube and the following stepwise heating cycle is employed.

The material is heated to a temperature of about  $200^\circ\text{C}$ . in a period of about 10 hours. The temperature is maintained at  $200^\circ\text{C}$ . for 24 hours after which time the temperature is gradually raised to about  $250^\circ\text{C}$ . over a 2 hour temperature interval. The temperature is maintained at  $250^\circ\text{C}$ . for about 24 hours after which time the temperature is gradually increased to  $338^\circ\text{C}$ . over about a 2 hour period. The temperature is held at  $338^\circ\text{C}$ . for 72 hours after which time the product is cooled to room temperature.

##### EXAMPLE III

11,350 grams of chromium trioxide is heated in a Pyrex tube in a vertical resistance furnace. An atmosphere of pure oxygen gas is maintained in the heating vessel by a continuous flow of about 0.5 cubic feet per hour of oxygen through the vessel. The temperature of the contents is monitored by thermocouples placed at the top, middle and bottom of the contents in the Pyrex tube so as to insure temperature control in order to prevent heating spikes of the contents of greater than about 15 degrees centigrade during the heating cycle. A stepwise heating cycle is followed. The heating cycle is described with reference to the table below which indicates the temperature of the reactants as measured by the middle thermocouple, the temperature at which the furnace is set and the number of hours of each temperature interval.

Reaction Temperature, °C.	Temperature of Furnace, °C.	Hours
0—200	215	10
200	215	62
200—220	215—225	4
220	225	68
220—235	225—240	4
235	240	20
235—240	240—245	4
240	245	20
240—250	245—255	4
250	255	20
250—260	255—270	4
260	270	20
260—280	270—290	4
280	290	20
280—300	290—310	4
300	310	20
300—325	310—335	4
325	335	20
325—340	335—345	4
340	345	68

(b) Preparation of Ferromagnetic Chromium Dioxide from Chromium Pentoxide.

EXAMPLE IV

A slurry consisting of 38 grams of chromium pentoxide prepared as in Example I, 15.2 grams of water and 0.19 grams of antimony trioxide ( $\text{Sb}_2\text{O}_3$ ) is placed in a quartz tube, which tube is inserted in an open tube hydrothermal pressure vessel constructed of A—286 alloy, and having an internal volume of 75 cubic centimeters.

The slurry is first pressurized to a pressure of 545 atmospheres under argon at room temperature. The pressure vessel is then heated as follows: The temperature is raised from room temperature to about 200°C. in the period of one hour. The temperature is then held at 200°C. for an additional hour, after which time the temperature is increased to 350°C.

over a period of about a half hour. The temperature is held at 350°C. for three hours after which time the temperature is allowed to cool to room temperature.

The product is ferromagnetic chromium dioxide. This product is washed several times with distilled water and then by acetone and dried at 70°C. in air. The material is then reduced to a free flowing powder in a Waring blender.

EXAMPLE V

A slurry consisting of 1390 grams of chromium pentoxide prepared as recited in Example II, 555 grams of water and 6.9 grams of antimony trioxide is placed in a stainless steel cannister which is inserted into a 2 liter A—286 alloy hydrothermal pressure

vessel. The pressure apparatus is of the type having an AE seal closure as is known in the art. The pressure vessel is then charged under an argon atmosphere to a pressure of 454 atmospheres. The pressure vessel and its contents are then heated as follows: The temperature is raised from 25°C. to 53°C. in 10 minutes, from 53°C. to 133°C. over a 35 minute period, from 133°C. to 186°C. over a 30 minute period, from 186 degrees C. to 249°C. over a 30 minute period, from 249°C. to 307°C. over a 30 minute period and 307°C. to 338°C. over a 30 minute period, from 338°C. to 343°C. over a 30 minute period, and then the temperature is held at 340°C. for 2 hours and 45 minutes after which time the temperature is allowed to cool to room temperature. At the maximum temperature the maximum pressure reached was about 24,750 psi.

After cooling to room temperature, the resultant ferromagnetic chromium dioxide is removed from the pressure vessel and washed and filtered with deionized water until no color is observable in the filtrate. The material is then washed with acetone and dried at 70°C. The chromium dioxide is then reduced to a free flowing powder in a Waring blender.

#### EXAMPLE VI

A slurry is prepared consisting of 90 grams of chromium pentoxide made in accordance with Example III, 36 grams of water and 0.45 grams of antimony trioxide. The slurry is placed in a quartz tube which is inserted into a cylindrical hydrothermal pressure vessel of 160 cm<sup>3</sup> volume which employs an AE seal device. The tube is pressurized under argon to about 615 atmospheres. The pressure vessel and its contents are then heated as follows: The temperature is first raised from room temperature to 59°C. in 15 minutes and then from 59°C. to 158°C. in a 45 minute period, and then from 158°C. to 200 degrees C. in a 30 minute period. The temperature is maintained at 200°C. for one hour after which time the temperature is increased to 280°C. in a 15 minute period and then to 336°C. in a second 15 minute period and finally to a temperature of 345°C. in an additional 5 minute period. The temperature is held at 345°C. for one hour, after which time the pressure vessel is cooled to room temperature and the resulting ferromagnetic chromium dioxide removed. The chromium dioxide is washed, dried, and blended as described with reference to Example V. The maximum pressure reached during the heating cycle is 1628 atmospheres.

Typically the saturation moment of the magnetic chromium dioxide powder prepared according to the above examples at room temperature is about 5300±200 gauss for material of coercivities in the range of from 300—650 oersteds. The coercivity of a bulk

powder is about 85% of that measured on tape.

The amount of water and/or antimony trioxide used in the preparation of chromium dioxide affects the coercivity of the resultant chromium dioxide. The coercivity decreases with increasing amounts of water in the range of 20 weight percent to 40 weight percent of water and then becomes almost constant in the range of 40 weight percent to 60 weight percent of water. It is therefore preferable to use about 40 weight percent of water since the use of this amount will allow an increased amount of chromium dioxide to be prepared in a given size reaction vessel as compared to greater amounts of water. In addition, the coercivity can be made reproducible as there is little change in coercivity when using about 40 weight percent water. Furthermore, as the water content is decreased below 40 weight percent, the resultant material becomes harder and more difficult to remove from the container at the end of the run.

The coercivity of the ferromagnetic chromium dioxide varies approximately linearly with the concentration of the antimony trioxide used in the preparation of the chromium dioxide. In order to produce chromium dioxide having coercivities preferred for magnetic recording tapes, one typically includes from 0.2 to 1 weight percent antimony trioxide although greater amounts can be employed.

A preferred range of pressures useful in the open tube hydrothermal preparation of chromium dioxide from chromium pentoxide is from 1,000 atmospheres to 1,800 atmospheres at maximum temperatures of from 300°C. to 400°C.

The pressure vessels are placed under inert gas pressures of 390 to 520 atmospheres prior to heating the vessel. It is also preferred to employ heating rates which do not exceed 2° per minute when preparing the chromium dioxide.

It is further preferred that during the preparation of chromium dioxide from the pentoxide, that the temperature of the pressure vessel be held at a temperature of about 200°C. for a period of time sufficient to allow substantially all the reactants to form an aqueous solution. This time will vary with the size and composition of the batch and generally requires approximately one hour. It has also been found preferable to maintain the pressure vessel at a temperature of 350°C. for at least one hour prior to cooling.

#### (c) Tape Coating Procedure

Magnetic tape is prepared from chromium dioxide in the following manner. A tape coating is prepared by dispersing about 20 grams of chromium dioxide in a vinyl copolymer formulation such as a type commonly used in the prior art in the production of audio tape.

The volume loading of the magnetic material is about 40%. The magnetic materials, binder formulation, and solvents are charged into a small laboratory type sand mill, and milled for about 17 hours. The resultant dispersion is then filtered and coated to a thickness of about 0.33 mils on a polyester base. About 60 feet of tape is coated by this procedure. The tape is then dried and thereafter slit into 1/4 inch widths for use.

Tapes prepared as above were measured for thickness of coating, magnetic properties, and recording characteristics. Coercivity, retentivity, and orientation (ratio of the retentivity to flux density at 1000 oersteds) are determined from hysteresis traces. Recording data were taken on an Ampex 300—2U 1/4 track recorder, at 3 3/4 inches per second tape speed and are presented in Table I. The recorder employs gap lengths of 350 micro inches for recording and 90 micro inches for playback. Recording pre-emphasis of 19 db from 1 kHz to 15 kHz was used. Playback compensation was adjusted to give uniform performance for RCA 12A—64T tape standard.

The following is a brief explanation of terms which define some of the principal recording characteristics: (1) peak bias, the bias current giving maximum response for 15 mil wavelength recording; (2) flat bias, the bias current giving equal response at 0.25 and 15

mil wavelength recordings; (3) sensitivity at peak bias, the maximum response for 15 mil wavelength recording; (4) sensitivity at flat bias, the response at flat bias; (5) relative response, the difference in response between 15 mil and 0.25 mil wavelength recordings at peak bias; (6) maximum short wavelength sensitivity, the maximum response for 0.25 mil wavelength recording. The constant record current was obtained by using an input signal of 0.2 V for each wavelength. The broadband bias noise (300 Hz—20 kHz), is the RMS output level in record mode with no signal and the overload output, is the signal level at 2% 3rd harmonic distortion for 15 mil wavelength. The signal to noise ratio is the difference between overload output and the broadband bias noise.

Table I presents recording and other characteristics of magnetic tape comprising CrO<sub>2</sub> prepared in accordance with Examples IV, V, and VI, respectively. It also includes for comparison tape characteristics of tape (x and y) prepared in the same manner as the aforementioned tape but comprised of magnetic dioxide prepared from chromium pentoxide wherein there was a temperature overshoot or spike of greater than 15°C. during the preparation of the pentoxide.

It can be seen from the table that the broadband bias noise is about 3 db lower for tape comprised of chromium dioxide which was made in accordance with the invention.

TABLE I  
Recording Data from 1/4" Width Magnetic Tapes

	Ex. 4	Ex. 5	Ex. 6	X(c)	Y(c)
CrO <sub>2</sub> batch as in Coating thickness (Mils)	.303	330	.326	.342	.343
Tape coercivity (oersteds)	448	440	498	430	455
Tape retentivity (gauss)	1600	1680	1590	1600	1690
Orientation	.90	.92	.93	.93	.92
Flux per 1/4 in. tape width (maxwells)	.78	.89	.84	.88	.94
Overload output, peak bias (a)	12.3	14.0	13.6	14.0	14.8
Overload output, flat bias (a)	12.0	14.0	13.6	13.9	14.1
Broad-band bias noise (b)	-52.8	-50.9	-52.4	-49.7	-48.4
Signal-to-noise ratio, peak bias (dB)	65.4	64.9	66.0	63.7	63.2
Signal-to-noise ratio, flat bias (dB)	65.3	64.9	66.0	63.6	62.5
Sensitivity, peak bias (b)	12.5	12.0	13.2	12.4	11.8
Sensitivity, flat bias (b)	12.5	12.0	13.3	12.4	12.0
Maximum short wavelength sensitivity	7.5	3.5	5.5	6.5	6.5
Relative response (dB)	-0.8	+1.5	+2.3	-1.3	-2.0

(a) in dB above 1V, 600 ohm.

(b) in dB below 1V, 600 ohm.

(c) During the preparation of the Cr<sub>2</sub>O<sub>3</sub> used in making the CrO<sub>2</sub> of these tapes there were temperature spikes of about 25° C. — 65° C. above the control temperature in X and from 40° C. to 75° C. in Y. The chromium pentoxide of Y had green Cr<sub>2</sub>O<sub>3</sub> at the bottom of the reaction tube. This portion was discarded prior to conversion to the CrO<sub>2</sub>.

- 5 It has been found that magnetic chromium dioxide prepared in accordance with the disclosed process has a particle size distribution which is more favorable than chromium dioxide otherwise prepared. Curve 1 of Figure 1 is a histogram of chromium dioxide prepared as in Example 4 above and curve 2 is a histogram of chromium dioxide indicated as CrO<sub>2</sub>=X in Table I. The latter chromium dioxide was prepared from chromium pentoxide in which there was temperature excursions of greater than 15°C. during the preparation of the pentoxide. The histograms plot frequency of observation against particle size in microns. It can be seen from the histogram that the chromium dioxide prepared in accordance with Example 4 has a much narrower particle size distribution curve than that of the other chromium dioxide. The curve is skewed somewhat toward the left and may be approximately represented by the formula
- 10
- 15
- 20

$$f(x) = \frac{1}{\alpha! \beta(\alpha+1)} x^\alpha e^{-x/\beta}$$

where  $\alpha$  and  $\beta$  are the distribution parameters,  $f(x)$  is the distribution function (in this case the frequency of observation), and  $x$  is the independent variable, particle length. Figure 2 is a plot of the length to width ratio versus the frequency of observation of the same samples as presented in Figure 1. It can be seen from this graph that the acicularity of the chromium dioxide made in accordance with Example IV (curve 3) covers a much narrower range of length to width ratios than that of sample X (curve 4). The peak of the length to width ratio as indicated by this graph is about 8.

Figure 3 is a plot of the chromium dioxide particle length, in microns, against the cumulative frequency of observations, in percent. This means that all particles having a length at or lower than any specific length will be included in obtaining the cumulative frequency of observations. This Figure shows three curves. Curve 5 is a vertical line which represents the most ideally desirable curve wherein all particles are of one length. Curve 6 is a curve of particles as prepared in accordance with Example IV and presented in Figures 1 and 2. Curve 7 is a curve obtained from examining Sample X. Curve 6 is typical of chromium dioxide prepared in accordance with the invention. This curve has a linear portion having a slope of 250 microns<sup>-1</sup>, in which slope can be said to characterize the chromium dioxide particles made in accordance with the invention herein. In addition there are almost no particles having a particle length of greater than 0.9 micrometers.

#### WHAT WE CLAIM IS:—

1. A method of preparing chromium pentoxide, comprising heating chromium trioxide at atmospheric pressure in an atmosphere containing free oxygen with a temperature schedule controlled such that no part of the heated mass ever has a temperature more than 15°C. above the control temperature, said control temperature not exceeding 350°C.

2. A method of preparing chromium pentoxide, as claimed in claim 1, wherein said heating is performed in a controlled series of stages.

3. A method as claimed in claim 1 or 2, of preparing chromium pentoxide comprising heating and maintaining chromium trioxide at its melting point until said chromium trioxide is completely melted, whereat said chromium trioxide undergoes decomposition to other chromium oxides; slowly heating and maintaining the decomposing chromium trioxide at a temperature of from 196°C. to 250°; slowly heating the chromium oxide further to about 340°C.; and maintaining this temperature of about 340°C. until essentially all the chromium oxides are converted to chromium pentoxide.

4. A process for the preparation of ferro-

magnetic chromium dioxide from chromium pentoxide prepared by the method described in claim 1, 2 or 3, comprising forming a slurry of the chromium pentoxide containing antimony trioxide and water, placing the slurry in an open tube pressure vessel, applying to said vessel a pressure of 390—520 atmospheres and heating said slurry to a temperature sufficient to hydrothermally decompose said chromium pentoxide to form said chromium dioxide.

5. A process as claimed in claim 4, wherein said antimony trioxide is present as 0.2 to 1 weight percent and water comprises 20 to 60 weight percent of the slurry mixture.

6. A process as claimed in claim 4 or 5, including the step of placing the slurry under an inert gas pressure of from 390 to 520 atmospheres prior to said heating, the subsequent temperature being from 300°C. to 400°C. and the pressure from 1100 to 1800 atmospheres.

7. A process as claimed in claim 6, wherein the rate of heating does not exceed 2°C. per minute.

8. A process as claimed in any one of claims 4, to 7 wherein the temperature of the pressure vessel is held at 200°C. for a period of time sufficient to allow substantially all the reactants to form an aqueous solution.

9. A process as claimed in any one of claims 4 to 7, wherein the pressure vessel is held at 350°C. for at least one hour prior to cooling.

10. A process as claimed in any one of claims 4 to 9 wherein the slurry contains about 40 percent by weight of water.

11. A ferromagnetic chromium dioxide prepared by the process described in any one of claims 5 to 10 having a coercive force of from 300 to 650 oersteds, a saturation magnetization of from 5,000 to 5,600 oersteds and a particle size distribution approximately as represented by the following formula:

$$f(x) = \frac{1}{\alpha! \beta(\alpha+1)} x^\alpha e^{-x/\beta}$$

wherein  $f(x)$  is the frequency of observation,  $x$  is the particle length in microns and  $\alpha$  and  $\beta$  are distribution parameters, and wherein a curve plotting particle size length, in microns as abscissa versus the cumulative frequency of observations as ordinate has a linear portion having a slope of 250 or greater.

12. A magnetic recording element comprising ferromagnetic chromium dioxide of the type described in claim 11 dispersed in a binder and coated upon a base.

13. A method of preparing chromium pentoxide substantially as in any one of Examples I to III.

14. A process for the preparation of ferromagnetic chromium dioxide substantially as in any one of Examples IV to VI.

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For the Applicants:  
MATTHEWS, HADDAN & CO.,  
Chartered Patent Agents,  
Haddan House,  
33 Elmfield Road,  
Bromley BR1 1SU.

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